<Division of Environmental Chemistry>Solution and Interface Chemistry

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– Solution and Interface Chemistry –

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Scope of Research

To understand the chemical structure and properties of a molecular aggregated system, the keywords of molecular interactions and orientation are focused on, and the molecular aggregates are investigated by using originally developed spectroscopic techniques. The current major topics are: (1) perfluoroalkyl-specific properties in a condensed system and a single molecule; (2) controlling factors of a molecular packing and orientation in a thin film of an organic semiconductor compound; (3) the optimal experimental condition and the correction factor of pMAIRS based on electrodynamics for estimating an accurate quantitative molecular orientation in a thin film having a surface roughness.

KEYWORDS

Infrared and Raman Spectroscopy
Perfluoroalkyl Compounds
pMAIRS
Surface and Interface Chemistry
Organic Semiconductor

Selected Publications

Wakai, C.; Shimoaka, T.; Hasegawa, T., Characterization of Adsorbed Molecular Water on the Surface of a Stretched Polytetrafluoroethylene Tape Analyzed by ^{1}H NMR, *J. Phys. Chem. B*, **120,** 2538-2543 (2016).

Shimoaka, T.; Tanaka, Y.; Shioya, N.; Morita, K.; Sonoyama, M.; Amii, H.; Takagi, T.; Kanamori, T.; Hasegawa, T., Surface Properties of a Single Perfluoroalkyl Group on Water Surfaces Studied by Surface Potential Measurements, *J. Colloid Interf. Sci.*, **483,** 353-359 (2016).

Hada, M.; Shioya, N.; Shimoaka, T.; Eda, K.; Hada, M.; Hasegawa, T., Comprehensive Understanding of Structure-Controlling Factors of a Zinc Tetraphenylporphyrin Thin Film Using pMAIRS and GIXD Techniques, *Chem. Eur. J.*, **22,** 16539-16546 (2016).

Shimoaka, T.; Hasegawa, T., Molecular Structural Analysis of Hydrated Ethylene Glycol Accounting for the Antifreeze Effect by Using Infrared Attenuated Total Reflection Spectroscopy, *J. Mol. Liquids*, **223,** 621-627 (2016).

Iwasa, J.; Kumazawa, K.; Aoyama, K.; Suzuki, H.; Norimoto, S.; Shimoaka, T.; Hasegawa, T., In Situ Observation of a Self-Assembled Monolayer Formation of Octadecyltrimethoxysilane on a Silicon Oxide Surface Using a High-Speed Atomic Force Microscope, *J. Phys. Chem. C*, **120,** 2807-2813 (2016).

Characterization of Adsorbed Molecular Water on the Surface of a Stretched Polytetrafluoroethylene Tape Analyzed by ^{1}H NMR

A single molecule often exhibits a largely different material character from a bulk matter. Although a perfluoroalkyl (Rf) compound is a representative one, many interests have mostly been devoted to the bulk character only thus far, leaving the single molecular character unclear. Recently, a new theoretical framework, stratified dipole-arrays (SDA) theory, has appeared for comprehensive understanding of Rf compounds in terms of both single and bulk systems. On this theory, a mechanically stretched polytetrafluoroethylene (PTFE) is expected to exhibit a single-molecular character having dipole-driven properties, which should attract molecular water. In the present study, a stretched PTFE tape is revealed to attract molecular water (not water droplet) in fact, and the adsorbed water molecules are highly restricted in motion by the dipole−dipole interaction studied by using ^{1}H NMR, which agrees with the prediction by the SDA theory.

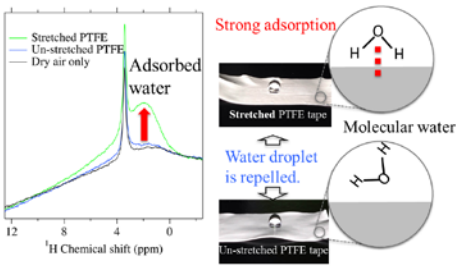

Figure 1. ^{1}H NMR spectra of strongly adsorbed molecular water on a stretched PTFE tape.

Surface Properties of a Single Perfluoroalkyl Group on Water Surfaces Studied by Surface Potential Measurements

A discriminative study of a single perfluoroalkyl (Rf) group from a bulk material is recently recognized to be necessary toward the total understanding of Rf compounds based on a primary chemical structure. The single molecule and the bulk matter have an interrelationship via an intrinsic two-dimensional (2D) aggregation property of an Rf group, which is theorized by the stratified dipole-arrays (SDA) theory. Since an Rf group has dipole moments along many C–F bonds, a single Rf group would possess a hydrophilic-like character on the surface. To reveal the hydration character of a single Rf group, in the present study, surface potential (ΔV) measurements are performed for Langmuir monolayers of Rf-containing compounds. From a comparative study with a monolayer of a normal hydrocarbon compound, the hydration/dehydration dynamics of a lying Rf group on water has first been monitored by ΔV measurements, through which a single Rf group has been revealed to have a unique "dipole-interactive" character, which enables the Rf group interacted with the water 'surface.' In addition, the SDA theory proves to be useful to predict the 2D aggregation property across the phase transition temperature of 19 °C by use of the ΔV measurements.

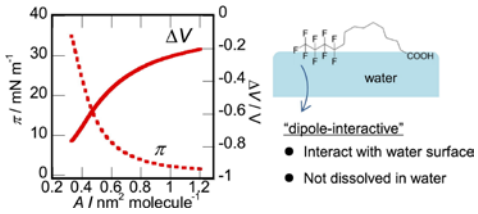

Figure 2. Schematic image of a dipole-interactive Rf group on the water surface and a fairly large negative surface potential.

Comprehensive Understanding of Structure-Controlling Factors of a Zinc Tetraphenylporphyrin Thin Film Using pMAIRS and GIXD Techniques

The performance of an organic electronic device is significantly influenced by the anisotropic molecular structure in the film, which has long been difficult to predict especially for a solution process. In the present study, a zinc tetraphenylporphyrin (ZnTPP) thin film prepared by a solution process was chosen to comprehensively explore the molecular-arrangement mechanism as a function of representative film-preparation parameters: solvent, film-preparation technique, and thermal annealing. The anisotropic structure was first analyzed by using a combination of infrared p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) and grazing incidence X-ray diffraction (GIXD), which readily revealed the molecular orientation and crystal structure, respectively. As a result, the real dominant factor was found to be the evaporation time of the solvent that determines the initial two different molecular arrangements, types-I and -II, while the thermal annealing was found to play an additional role of improving the molecular order. The correlation between the molecular orientation and the crystal structure was also revealed through the individual orientation analysis of the porphyrin and phenyl rings.

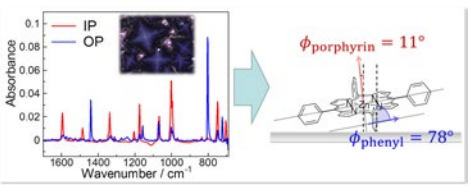

Figure 3. pMAIRS spectra of a ZnTPP thin film and a schematic image of the two conjugated rings on the surface.